Syntheses and evaluations of three sulfonated polycondensate dispersants for coal–water slurries

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A R T I C L E   I N F O

Article history:
Received 11 March 2013
Received in revised form 17 December 2013
Accepted 24 January 2014
Available online 3 February 2014

Keywords:
Coal–water slurry
Sulfonated polycondensate
Dispersant
Adsorption

A B S T R A C T

Three sulfonated polycondensate dispersants—sulfonated aceto-formaldehyde (SAF), sulfonated phenol-formaldehyde (SPF) and sulfonated 2-naphthol-formaldehyde (SNF), were synthesized and applied as the dispersants for the coal–water slurries (CWSs) prepared from Chinese Shenfu coal. The CWS application performance investigations show that SNF can most effectively reduce CWS viscosity, but SAF has the best ability in stabilizing CWS. The physicochemical property investigations of the three dispersants show that the adsorption amount of SAF at coal–water interface is greater than those of SPF and SNF, and SAF has the greatest capacity in charging coal surface with electronegativity, but SNF has better wetting property than SPF and SAF on coal surface. It is indicated that the capabilities of the tested dispersants depend not only on the hydrophobic group character but also on the molecular flexibility. Based on the above, the principle of stabilization of the CWSs prepared from the three dispersants is presented.

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1. Introduction

In recent years, due to the rapid depletion of petroleum oil, many studies have been performed particularly on coal–water slurry (CWS) which has been regarded as a promising alternative to petroleum [1–3]. A desirable CWS should have such properties as a high coal content for economic consideration, an excellent stability for storage and a viscosity as low as possible for transportation and combustion. To achieve the demands, the selection of a dispersant plays an extremely important role [4,5].

Currently, the anion polymer dispersants are considered as the major type of the dispersants for CWS. Many researches have discovered that the hydrophilic sulfonic group in an anion dispersant and its molecular weight have large influences on the performance of CWS [6–9]. Furthermore, the chemical structure of an anion dispersant is also a major determining parameter affecting CWS properties. However, for an anion dispersant, the effects of the hydrophobic group character and the molecular flexibility on CWS performance have not been well documented.

In this study, three sulfonated polycondensates with similar chemical structures—sulfonated aceto-formaldehyde (SAF), sulfonated phenol-formaldehyde (SPF) and sulfonated 2-naphthol-formaldehyde (SNF), were synthesized and applied as the dispersants for the CWSs prepared from Chinese Shenfu coal. The CWS application properties such as viscosities and stabilities, were investigated in the presence of the three dispersants. The physicochemical characteristics of the three dispersants at coal–water interfaces, including contact angles, adsorption amounts and zeta potentials, were also examined. This study has discussed the relationships between dispersant capabilities and hydrophobic group character, molecular flexibility. Based on the investigations, the principle of stabilization of the CWSs prepared from the tested dispersants is presented.

2. Experimental

2.1. Materials

The raw materials used to synthesize the dispersants are as follows: analytical grade phenol, analytical grade 2-naphthol, analytical grade anhydrous sodium sulfite, chemically pure formaldehyde (37%), chemically pure acetone, chemically pure concentrated sulfuric acid (98%) and chemically pure sodium hydroxide.

Shenfu coal from Shenfu, Shaanxi Province in China, a kind of non-caking coal, was used in this study. Table 1 shows the results of the proximate and ultimate analyses of the coal. The coal was uninterruptedly comminuted in a dry ball mill to obtain a coal powder, then the coal powder was screened and formed coal sample according to the multi-peak grade blending technology of Texaco. The particle size distribution of the coal sample is given in Table 2.

2.2. Syntheses and purification of SAF, SPF and SNF

The deionized water and anhydrous sodium sulfite were mixed in a reactor flask equipped with a temperature-controlled electric heating device, a motor stirrer, a reflux condenser and a dropping funnel. The
temperature was raised to 55 °C, then acetone was fed into the reactor, and the sulfonation reaction was carried out at 55 °C for 1 h. Afterwards, the temperature was raised to 85 °C, then formaldehyde was dropwise added into the reactor, and the polycondensation was kept at 85 °C for 4 h. At the end of the reaction, the reaction liquid was cooled to room temperature, then the pH value was adjusted to around 7 using 30 wt.% sodium hydroxide solution, and the SAF product was obtained.

In a reactor flask equipped with a temperature-controlled electric heating device, a motor stirrer, a reflux condenser and a dropping funnel, phenol was melted at 70 °C for 30 min, then concentrated sulfuric acid was uniformly dropped into the reactor, and sulfonation reaction was performed at 95 °C for 3 h. Thereafter, formaldehyde was dropwise added into the reactor and the polycondensation was maintained at 95 °C for 3 h. At the end of the reaction, the reaction mixture was cooled to room temperature, then the pH value was adjusted to approximately 7, and the SPF product was obtained.

The 2-naphthol was fed in another reactor flask. The temperature was raised to 130 °C, then concentrated sulfuric acid was dropwise added into the reactor, and sulfonation reaction was maintained at 130 °C for 3 h. Afterwards, formaldehyde was uniformly dropped into the reactor and the polycondensation was kept at 130 °C for 3 h. At the end of the reaction, the reaction liquid was cooled to room temperature, then the pH value was adjusted to about 7 using 30 wt.% sodium hydroxide solution, and the SNF product was obtained.

The above-mentioned three polycondensation solutions were precipitated by ethanol, respectively, and the residues were dried in an oven at 80 °C to constant mass.

2.3. Methods

2.3.1. Infrared spectrum analyses

The FT-IR spectra in the range of 4000–400 cm\(^{-1}\) were recorded on a spectrophotometer (VECTOR-22, Bruker, Germany). The spectra were obtained by employing potassium bromide pellet technique.

2.3.2. TG analysis

TG analysis was carried out on a thermogravimetric analyzer (Q500, TA Instrument Company, USA) in nitrogen atmosphere at a heating rate of 10 °C/min.

2.3.3. Viscosity measurement and rheological property determination

Viscosity measurement was performed by using a rheometer (AR-2000, TA Instrument Company, USA). The CWS was agitated at 1200 rpm for 10 min before the measurement. The temperature was kept within 25 ± 1 °C. The measured viscosity value is the apparent viscosity.

2.3.4. Static stability test

The CWS prepared was poured into a glass cylinder (3 cm in diameter; CWS layer 15 cm in height). The top of the cylinder was sealed and the CWS was stored at room temperature for a definite period. The static stability of the CWS was evaluated by applying the rod penetration method [10].

2.3.5. Adsorption amount measurement

In adsorption test, the CWS was prepared with 10 wt.% of coal and known concentration of a dispersant. The slurry was stirred at 1200 rpm for 10 min, then centrifuged, and the supernatant was used for determining dispersant equilibrium concentration, employing an UV−vis spectrophotometer (UV-265FW, Shimadzu Corp., Japan). The concentration of the dispersant in the solution was determined from the characteristic absorption wavelength according to a predetermined calibration curve. The adsorption amount was calculated as follows:

\[
\Gamma_i = (C_{oi} - C_{fi}) V / m
\]

where \(\Gamma_i\) is the adsorption amount per unit mass coal (mg·g\(^{-1}\)), \(C_{oi}\) and \(C_{fi}\) are the initial and final mass concentrations of the dispersant (mg·L\(^{-1}\)), \(V\) is the total volume of the solution (L) and \(m\) is the mass of the coal sample (g).

2.3.6. Contact angle measurement

The contact angle was measured by applying the static drop method employing a drop shape analyzer (Easydrop, Kruss Company, Germany). The surface of small lump coal was burnished smoothly before the measurement. The static contact angle was obtained from the water droplet on coal surface, and then the photograph of the coal−water interface was taken. The mean value of the contact angle, which was measured five times, is used in this study.

2.3.7. Zeta potential measurement

The zeta potential of the coal particles in the CWS was determined by a zetasizer (ZEN3690, Malvern Instruments Corp., USA). The CWS was prepared by dispersing 0.1 g coal sample into 50 mL of the dispersant solution with a definite concentration and stirred by an agitator for 10 min. The average value of the zeta potential, which was measured three times at neutral pH, is adopted in this study.

3. Results and discussion

3.1. FT-IR analyses

The FTIR spectra of SAF, SPF and SNF are represented in Fig. 1. In Fig. 1a, the bands in the vicinity of 3441, 2927 and 1603 cm\(^{-1}\) are assigned to \(v_{O-H}\), \(v_{C-H}\) (CH\(_2\)) and \(v_{C=O}\), respectively, and the characteristic stretching peaks of S−O could be seen at 1179 and 1044 cm\(^{-1}\). In Fig. 1b, the adsorption bands at 3445 and 2926 cm\(^{-1}\) correspond to \(v_{O-H}\) and \(v_{C-H}\) (CH\(_2\)), and the typical adsorption peaks of benzene ring emerge at 3002 (C−H), 1602 and 1503 cm\(^{-1}\), while the characteristic adsorption bands of S−O appear at 1117 and 1033 cm\(^{-1}\). In Fig. 1c, the bands at 3446 and 2924 cm\(^{-1}\) are assigned to \(v_{O-H}\) and \(v_{C-H}\).
and the typical adsorption peaks at 3058 (C–H), 1601 and 1500 cm$^{-1}$ should be derived from naphthalene ring. In short, all of the above results indicate that the three sulfonated polycondensate dispersants have the due structures as depicted in Fig. 2.

3.2. TG analysis

The thermal decomposition behavior of SAF, SPF and SNF was examined by TG analysis and the results are given in Fig. 3. As seen in the figure, every curve could be divided into two zones, and the first zone is attributed to the loss of adsorbed water, while the second weight loss corresponds to the decomposition of the polymer. The thermal decomposition initiated apparently at approximately 150 °C for SAF, 290 °C for SNF, and 400 °C for SPF, which suggests that SPF has excellent thermal stability and suitable for use in high temperature environment.

3.3. Viscosity and rheological characteristics of CWS

In order to evaluate the viscosity-reducing capacities of the three sulfonated polycondensate dispersants, the apparent viscosities of the CWSs with coal content of 65 wt.%, neutral pH and different dispersant dosages, are exhibited in Fig. 4.

As shown in the figure, for each one of the three dispersants, the apparent viscosity decreases abruptly with increasing dispersant dosage, reaches a minimum and then increases above a certain dosage. The minimum viscosity corresponds to the optimal dispersant dosage (0.45 wt.% for each of the three dispersants). Two factors could account for the viscosity increase above the optimal dispersant dosage. Firstly, the increase of the counter-ion density (Na$^+$) will compress electric double layers, reducing the relatively long-range electrostatic repulsive force. Secondly, the structure of the adsorbed polymer dispersant on particle surface will be compressed by the negative charge (SO$_3^-$) in free polymers, which reduces the short-range steric repulsive force between particles. Both reducing mechanisms increase the suspension viscosity [11].

It could be concluded that SNF has the best viscosity-reducing capacity among the three dispersants at the optimal dispersant dosage, which may be attributed to the strong polarized $\pi$ electron interaction between SNF and coal. At the dosage, the apparent viscosity of the CWS prepared from SNF gives a minimum of around 420 mPa·s. Additionally, the apparent viscosity of the CWS prepared from SAF is less than that of the CWS prepared from SPF at 0.45 wt.% dispersant dosage, which may be due to the larger steric repulsive force between particles that resulted from the flexible structure of the SAF molecule.

The rheological behavior of CWS is an important factor to affect its performance. In this study, the other preparation conditions were the same as the above, the CWSs with the dispersant dosage of 0.45 wt.% were prepared. The apparent viscosity/shear rate dependence curves of the CWSs are depicted in Fig. 5. The equivalent shear stress/shear rate data for each CWS are fitted to the Herschel–Bulkley model and

![Fig. 1. FTIR spectra of (a) SAF, (b) SPF and (c) SNF.](image1)

![Fig. 2. Molecular structures of (a) SAF, (b) SPF and (c) SNF.](image2)

![Fig. 3. TGA curves of SAF, SPF and SNF.](image3)

![Fig. 4. Effect of dispersant dosages on apparent viscosities at shear rate of 100 s$^{-1}$.](image4)
the results are reported in Table 3. The Herschel–Bulkley model is as follows:

\[ \tau = \tau_y + K \gamma^n \]

where \( \tau \) is the shear stress, \( \tau_y \) is the yield stress, \( K \) is the fluid consistency index, \( \gamma \) is the shear rate and \( n \) is the flow behavior index.

As shown in Fig. 5 and Table 3, all the CWSs prepared from different dispersant exhibit shear-thinning characteristic, the flow behavior indexes for all the CWSs are less than 1, which indicates that the CWSs belong to pseudoplastic fluid.

3.4 Static stability of CWS

The purpose of this study is to investigate the stabilization properties of the CWSs prepared from the three sulfonated polycondensate dispersants. All CWSs were prepared at neutral pH and 0.45 wt.% dispersant dosage, and the storage time was 72 h. The results of the penetration ratios examined are expressed in Table 4.

As seen in the table, the penetration ratio of the CWS prepared from each one of the three dispersants decreases with increasing coal content, but the CWS prepared from SAF has the highest penetration ratio at same coal content, which indicates the best ability of SAF in stabilizing CWS. This might be due to the flexible chain structure of SAF molecule.

3.5 Adsorption investigation

The dispersant molecules adsorbed on coal particles can modify their surface properties, decreasing particle–particle association, which is indispensable for the dispersion of the coal particles in water to prevent flocculation and agglomeration. The adsorption isotherms of the three sulfonated polycondensate dispersants on coal particles are illustrated in Fig. 6.

The figure shows that the adsorption amounts of SAF, SPF and SNF on coal surfaces increase markedly with increasing dispersant concentration at the beginning and then attain a plateau, which suggests that the adsorption curves exhibit monolayer adsorption characteristic [12]. Moreover, among the three dispersants, SAF has the highest adsorption amount on coal surface but the adsorption rate of SNF is the greatest.

Using Langmuir isotherm adsorption equation, the adsorption isotherms in Fig. 6 are fitted and the results are reported in Table 5. The Langmuir adsorption model is as follows:

\[ \Gamma / \Gamma_\infty = Kc / (1 + Kc) \]

where \( \Gamma \) is the adsorption amount (mg·g\(^{-1}\)), \( \Gamma_\infty \) is the saturated adsorption amount (mg·g\(^{-1}\)), \( c \) is the equilibrium mass concentration (mg·L\(^{-1}\)) and \( K \) is the Langmuir equilibrium constant. According to the table, the saturated adsorption amount of SAF is the highest and the Langmuir equilibrium constant of SNF is the largest, which testifies the highest adsorption amount of SAF and the greatest adsorption rate of SNF on coal surface.

For SNF, the driving force for the adsorption on coal is the intense polarized \( \pi \) electron interaction between the rigid naphthalene rings in the molecule and the fused aromatic rings in coal. The SNF molecule can be adsorbed to coal surface with its hydrophobic parts lying flat on the surface and the hydrophilic parts suspended in water. During adsorption process, the dispersant molecules seize continuously coal surface until a compact monolayer adsorption film emerges, covering almost all of coal surface (saturated adsorption). In this case, the intense polarized \( \pi \) electron interaction means a great adsorption rate of SNF and a compact adsorption film, simultaneity, the rigid chain character and the adsorption mode of lying flat result in a thin adsorption film and a low adsorption amount of SNF on coal surface.

The SPF molecule has similar adsorption action on coal surface to SNF molecule. Whereas the polarized \( \pi \) electron interaction is weaker than that in the case of SNF, which results in a relatively small adsorption rate of SPF and a relatively loose adsorption film, simultaneity,

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Fitted Herschel–Bulkley parameter values of CWSs prepared from SAF, SPF and SNF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersants</td>
<td>( \tau_y ) (Pa)</td>
</tr>
<tr>
<td>SAF</td>
<td>18.4268</td>
</tr>
<tr>
<td>SPF</td>
<td>24.7238</td>
</tr>
<tr>
<td>SNF</td>
<td>17.8293</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Penetration ratios of CWSs prepared from SAF, SPF and SNF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal content (wt.%)</td>
<td>Penetration ratio (%)</td>
</tr>
<tr>
<td>SAF</td>
<td>SPF</td>
</tr>
<tr>
<td>60.0</td>
<td>87</td>
</tr>
<tr>
<td>62.0</td>
<td>85</td>
</tr>
<tr>
<td>64.0</td>
<td>82</td>
</tr>
<tr>
<td>65.0</td>
<td>80</td>
</tr>
<tr>
<td>66.0</td>
<td>69</td>
</tr>
</tbody>
</table>

Fig. 6. Adsorption isotherms of SAF, SPF and SNF on coal.
the relatively flexible chain character results in a relatively thick adsorption film and a relatively high adsorption amount of SPF on coal surface.

For SAF, the driving forces for the adsorption on coal are the hydrophobic interaction, hydrogen bonding and ionic association between the aliphatic chains, hydroxyl groups, sulfonic groups in the molecule and the hydrophobic regions, hydrophilic regions on coal surface [13–15]. Nevertheless, the forces are much smaller than the polarized π electron interaction in the case of SNF and SPF, which causes a less adsorption rate and a looser adsorption film. Compared with SNF and SPF, SAF belongs to a flexible molecule which can be adsorbed on coal surface through randomly multi-point adsorption. Thus the adsorption film is thicker and the adsorption amount is higher.

3.6. Contact angle of surface of coal particle

The contact angle at coal–water interface reflects the average wettability property of coal surface [16]. In this study, the contact angles of the water and the dispersant solutions with the mass concentration of 0.45 wt.% on coal were measured and the results are given in Fig. 7.

As per the figure, the contact angle of the water on coal surface is 74.2°, and the SNF solution has minimal contact angle among the three dispersant solutions, which suggests that SNF has the best wetting ability on coal surface.

For the SNF dispersant, the strong polarized π electron interaction causes a compact adsorption film, and the hydrophilic regions on coal surface are effectively replaced by the hydrophilic groups of the dispersant molecules. It is considered that the superior wetting ability of SNF is derived from its relatively high density of the hydrophilic groups on coal surface. In the case of SPF, the weak polarized π electron interaction causes a loose adsorption film and a relatively low density of hydrophilic groups on coal surface. Thus the contact angle of the SPF solution on coal surface is greater than that of the SNF solution. As to SAF, the driving force for the adsorption on coal is minimal among the three dispersants, which brings about the loosest adsorption film and the most inferior wetting ability.

3.7. Zeta potential investigation

According to DLVO theory, the zeta potential of coal surface is an important factor affecting the dispersion and stabilization of the coal particles in water. The present study determines the effects of the three sulfonated polycondensate dispersants on the zeta potentials of coal surfaces and the results are shown in Fig. 8.

As seen in the figure, the zeta potential value of Shenfu coal surface is approximately —12 mV in the absence of dispersant, and the additions of the three dispersants could all increase the zeta potential absolute values of coal surface. With increasing dispersant concentration, the zeta potential absolute values increase sharply until 0.6–0.8 g L⁻¹, and drop slightly above the concentration range.

The adsorption amount of the dispersant has a significant influence on the zeta potential absolute value of coal surface. The adsorption amount increases with an increase of dispersant concentration before the saturated adsorption, which causes an increase of the negative charge number on coal surface and so an increase of zeta potential absolute value. Above the concentration of the saturation point, the excessive cations (Na⁺) from the dispersant are scattered in the diffusion layer, and the electronegativity of the coal surface is counteracted, and thus the zeta potential absolute value declines.

Besides, for SAF, SPF and SNF, the order of the zeta potential absolute values on coal surfaces is consistent with that of the adsorption amounts.

3.8. Principle of stabilization of CWS

Based on the above investigation results, the adsorption models of the three sulfonated polycondensate dispersants on coal surface are simulated in Fig. 9.

The SAF belongs to a flexible molecule, in which there are no obviously concentrated distribution areas of hydrophobic and hydrophilic groups. The hydrophilic groups on SAF molecule surface may undoubtedly hinder the aliphatic chains in the molecule adsorbed on the hydrophilic regions on coal surface via hydrophilic interaction. The aliphatic chains in SAF molecule can anchor on the hydrophobic regions on coal surface through randomly multi-point adsorption (see Fig. 9). Furthermore, the sulfonic groups in SAF molecule can anchor on the positively charged sites of coal surface via ionic association and the hydroxyl groups in the molecule can also anchor on the negatively charged sites of coal surface via hydrogen bonding. The above three interactions is weak, which causes a small adsorption rate and a loose adsorption.
film on coal surface. The loose adsorption film means that the SAF molecules cannot effectively occupy coal surface to enhance its surface wettability [17], which is disadvantageous to CWS stability. However, the flexible chain character and randomly multi-point adsorption mode result in a thick adsorption film and a large adsorption amount, which mean a powerful steric hindrance and a high zeta potential absolute value, respectively [18]. Both powerful steric hindrance and high zeta potential absolute value are advantageous to CWS stability. So, in spite of poor wettability, the SAF dispersant has the best capability in stabilizing CWS.

The SNF molecules contain a great quantity of the rigid naphthalene rings which form the evidently hydrophobic parts in the molecule. The naphthalene rings in SNF molecule have forceful affinity with the fused aromatic rings in coal due to the intense polarized π electron interaction, so the SNF molecule can be adsorbed to coal surface with its hydrophobic parts lying flat on the surface and the hydrophilic parts suspended in water. In this case, the intense polarized π electron interaction means a great adsorption rate of SNF and a compact adsorption film on coal surface. The compact adsorption film means that the SNF molecules can effectively seize coal surface to strengthen its surface wettability, which is advantageous to CWS stability. However, the rigid chain character and the adsorption mode of lying flat bring about a thin adsorption film and a small adsorption amount, which mean a weak steric hindrance and a low zeta potential absolute value, respectively. Both weak steric hindrance and low zeta potential absolute value are disadvantageous to CWS stability. So, in spite of good wettability, the SNF dispersant has the most inferior capability in stabilizing CWS.

The SPF molecule could also be adsorbed on coal surface by means of the polarized π electron interaction between the rigid benzene rings in the molecule and the fused aromatic rings in coal. Whereas the interaction is slightly weaker than that in the case of SNF, and the SPF molecule is slightly more flexible than the SNF molecule. So, compared with SNF, the SPF dispersant represents a slightly small adsorption rate, a slightly loose and thick adsorption film, a slightly inferior wettability, a slightly large adsorption amount, a slightly forceful steric hindrance, a slightly high zeta potential absolute value, and finally, a slightly good stability for CWS.

4. Conclusions

Three sulfonated polycondensates with similar chemical structures—SAF, SPF and SNF, were synthesized and applied as the dispersants for CWSs. The CWS application performance investigations show that SNF can most effectively reduce CWS viscosity and the slurry (coal content = 65 wt.% and dispersant dosage = 0.45 wt.%) exhibits around 420 mPa·s of apparent viscosity at 100 s⁻¹ of shear rate. SAF has the best ability in stabilizing CWS and the penetration ratio of the slurry prepared under the same conditions as the above is 80% within 72 h. The adsorption amount investigations of the three dispersants show that the order of the adsorption amounts at coal–water interfaces is SAF > SPF > SNF and the sequence of the adsorption rates is exactly contrary with that, which is proved by the obtained fitting parameters—saturated adsorption amount γ∞ and Langmuir equilibrium constant K. The large adsorption amount of SAF at coal–water interface could be attribute to its flexible molecular structure, and the great adsorption rate of SNF is derived from the intense polarized π electron interaction between the naphthalene rings in the molecule and coal. The zeta potential investigations of the three dispersants show the sequence of zeta potential absolute values is consistent with that of the adsorption amounts. But the results of contact angle examinations show that the order of contact angles is exactly contrary with that of the adsorption amounts. Both of the above cases result from the hydrophobic group character in the dispersant and the molecular flexibility.

The hydrophobic group character in the dispersant and the molecular flexibility greatly impacts on the adsorption amount, zeta potential and contact angle, and ultimately influences the dispersion and stabilization of CWS.

Acknowledgments

The authors express their sincere thanks for the financial supports provided by the National Natural Science Foundation of China (21176148, the National Natural Science Foundation of China (21303098) and the Doctor’s Scientific Subject Foundation of Shaanxi University of Science & Technology (Adsorption of polycarboxylate
dispersant on coal water interface and its interaction mechanism with coal. BJ13-04).

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